

Synthesis of Oxide Materials by Hydrothermal Hydrolysis of Aluminum Chloride Hexahydrate

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Abstract

In the present work, the processes of aluminum oxyhydroxides synthesis by hydrothermal hydrolysis in water solutions and in solid phase are considered. The process studies were conducted using a batch type autoclave at temperatures from 443 to 503 K at a pressure of 1.6 -2.3 MPa with the variation of such parameters as temperature, pressure, residence time of the reaction mixture in the reactor, flow velocity of the displacing gas during hydrolysis; number of washes, time and rate of hydrothermal decomposition products centrifugation, time and temperature of aluminium hydroxide drying. It is shown that Al-O-H product formed by hydrothermal hydrolysis of aluminum chloride hexahydrate $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, and urea jointly in water solutions is a highly dispersed (nano) γ -AlOOH (boehmite). Hydrothermal process of self-hydrolysis of aluminum chloride hexahydrate in solid phase with the use of crystalline water is lead to formation of bayerite (mainly) and aluminum oxychlorides with a total Cl content of not more than 4 %.

Keywords: alumina production, hydrolysis, hydrothermal synthesis, bayerite, boehmite.

1. Introduction

Currently, for the production of alumina from high-silicon raw materials, mainly kaolin, alkaline technologies are widely used. The proposed promising technologies are based on acidic methods for processing of kaolins and clays use sulfuric, hydrochloric and nitric acids, but they are multistage and high-cost [1].

The most advanced technology includes the leaching of raw materials with a solution of hydrochloric acid in an autoclave, separation of the resulting pulp, crystallization of aluminum chloride hexahydrate from clarified aluminum chloride solution with gaseous hydrogen chloride, calcining aluminum chloride hexahydrate to produce gamma-alumina and its final recrystallization in alkali solution to obtain metallurgical grade alumina. However, this technology can be significantly simplified by replacing the operations of crystallization and calcination of aluminum chloride hexahydrate by the decomposition operation to obtain aluminum hydroxide, which is directed to alkaline recrystallization. The method of hydrothermal hydrolysis of aluminum chloride hexahydrate is most suitable for replacing the existing energy-consuming multi-stage high-temperature methods of aluminum chloride decomposition [2].

The advantages of the hydrothermal hydrolysis method of producing Al-O-H products are:

1. Single-stage process;
2. Low energy consumption;
3. Chemical and phase purity of the product;
4. Low level of aggregation;
5. The ability to control the size, morphology and structure of the obtained Al-O-H products;
6. The possibility of using this method for high-silica raw materials of various origin.

Important features of the hydrolysis of aluminum chlorides in solutions at elevated temperatures (373-773 K) are [3]:

- (a) The incompleteness of the second and third hydrolysis steps;
- (b) The formation of soluble multicore aluminum oxychloride complexes forming colloidal solutions;
- (c) The strong dependence of the hydrolysis depth on the acidity of the medium and on the presence of additional components in the solution.

Based on the literature data, boehmite (or its modification - pseudo-boehmite) is the only Al-O-H product that can be obtained under mentioned hydrothermal conditions (temperature 433-513 K and pressure 0.6-2.4 MPa) in the presence of additional components that enhance hydrolysis. The output of boehmite is a quantitative estimate of the depth of hydrolysis of aluminum chloride. 100 % yield of boehmite indicates complete hydrolysis of aluminum chloride [4].

At the same time, there are no data about the possibility of hydrothermal hydrolysis with the production of Al-O-H products from crystalline aluminum chloride hexahydrate in solid phase—that is, in the process of self-hydrolysis involving lattice water of the crystalline hydrate.

The purpose of this work was to determine the possibility of carrying out the process of complete hydrolysis of aluminum chloride hexahydrate at elevated pressures and temperatures under hydrothermal conditions with the production of alumina products.

2. Experimental

The hydrolysis in water phase was performed under hydrothermal conditions with aqueous solutions of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (analytical grade with ≥ 98 % purity) with concentration of 3.0–30.0 wt. %, which was obtained from commercial source and used without purification. Carbamide of analytically pure grade with concentration of 8.5 – 20.2 wt % was served as an additive accelerating the hydrolysis. The solution volume was 30–60 mL. Experiments were performed at a temperature of 160 – 200 °C and pressure of 0.6–1.6 MPa in a 200-mL autoclave reactor, which was a part of the laboratory experimental setup, described early [5].

The characteristics of the installation enabled experiments on hydrothermal hydrolysis at temperatures of 423 – 523K and pressures of 0.1 – 5.0 MPa, with the measurement error and parameter adjustment accuracy of no worse than 3 % under the conditions of an inert gas flowing through the reactor. The pressure in the system was provided by the flow of argon delivered to the reactor inlet and varied with upstream and downstream high-pressure gas controllers, with the pressure corresponding to the saturated water vapor pressure at the prescribed temperature of experiment.

The reactor outlet was connected to a trap filled with distilled water to catch gaseous products carried away by the flow of argon. The argon flow rate was maintained constant and equal to $0.00125 \text{ m}^3 \text{ h}^{-1}$. The experiment duration was 1 to 10 h.

The resulting insoluble hydrolysis products were washed several times with distilled water, with the subsequent centrifugation of the sediment. The centrifugation was performed in the course of 8 min at a rotor speed of 2600 rpm. Further, the washed samples were dried at $T = 353 \text{ K}$ for 5 h. The composition and content of the insoluble precipitate was determined by weighing, X-ray fluorescence method, X-ray diffraction (XRD) analyses and ^{27}Al MAS NMR.

The hydrolysis in solid phase of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was performed within the same autoclave under the same temperature, pressure, duration, heating and cooling routines. The samples $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ weight was 15 g.

3. Results and Discussion

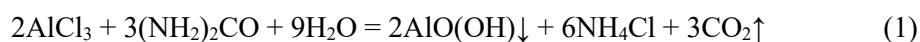
3.1. Hydrolysis in Water Solutions

Experiments conducted using a 5 – 20 % solutions of aluminum chloride at temperatures up to 513 K and pressures up to 2.4 MPa for 10 hours showed no boehmite formation under hydrothermal conditions. The main products of hydrolysis, apparently, can be various hydroxo complexes, polycations, or aluminum hydroxypolymers, the formation of which indicates the incompleteness of the hydrolysis of aluminum chloride. Attempts to accelerate the process of hydrolysis and initiate the formation of boehmite by removing the formed HCl from the reaction zone with a stream of displacing gas and increasing the temperature and pressure do not lead to the desired results.

The next stage of research was to study the effect of additives accelerating the hydrolysis on the depth of the hydrothermal decomposition process of the aluminum chloride solution. Ethanol, carbonate and sodium bicarbonate, thermally activated alumina, urea and others were used as additionally introduced components. As it turned out, the formation of boehmite during the hydrolysis of AlCl_3 without the introduction of additives does not occur under these conditions.

The use of seed heat-activated alumina also does not lead to the formation of boehmite. Adding ethanol to the solution allows, apparently, due to a gentle variation of pH from 3.0 to 4.9, to yield up to 11 % boehmite. Adding carbamide to the aluminum chloride solution turned out to be the most effective. In this case, the complete hydrolysis of AlCl_3 (above 99 %) was observed and pure boehmite was obtained.

Apparently, in the case of using a mixture of aluminum chloride and urea in water under hydrothermal conditions, the process of joint hydrolysis proceeds according to the equation (1):



It is known that the released ammonia slows down the hydrolysis of carbamide. There is also evidence that a change in the pH of the aluminum chloride solution to 6 – 7 results in the predominant formation of aluminum hydroxide during hydrolysis [6]. Thus, in our case, the carbamide hydrolysis is accelerated in the presence of AlCl_3 due to the interaction of ammonia with HCl released during the hydrolysis. At the same time, the hydrolysis of aluminum chloride is accelerated due to a pH shift to the alkaline side.

As it turned out, the complete hydrolysis of AlCl_3 at a temperature of 433-513 K and a pressure of 0.6 - 2.4 MPa with the yield of 100 % Al-O-H occurs at a small ratio $\text{AlCl}_3/(\text{NH}_2)_2\text{CO} = 0.67$. Samples of Al-O-H hydrolysis products obtained under these conditions were analyzed for chlorine content by the X-ray fluorescence method. The Cl content in the sample was 1.06 % (unwashed ammonium chloride). According to X-ray spectroscopy, DTA and high-resolution transmission electron microscopy, the product Al-O-H formed during hydrolysis is a highly dispersed γ -AlOOH (boehmite) (Fig. 1).

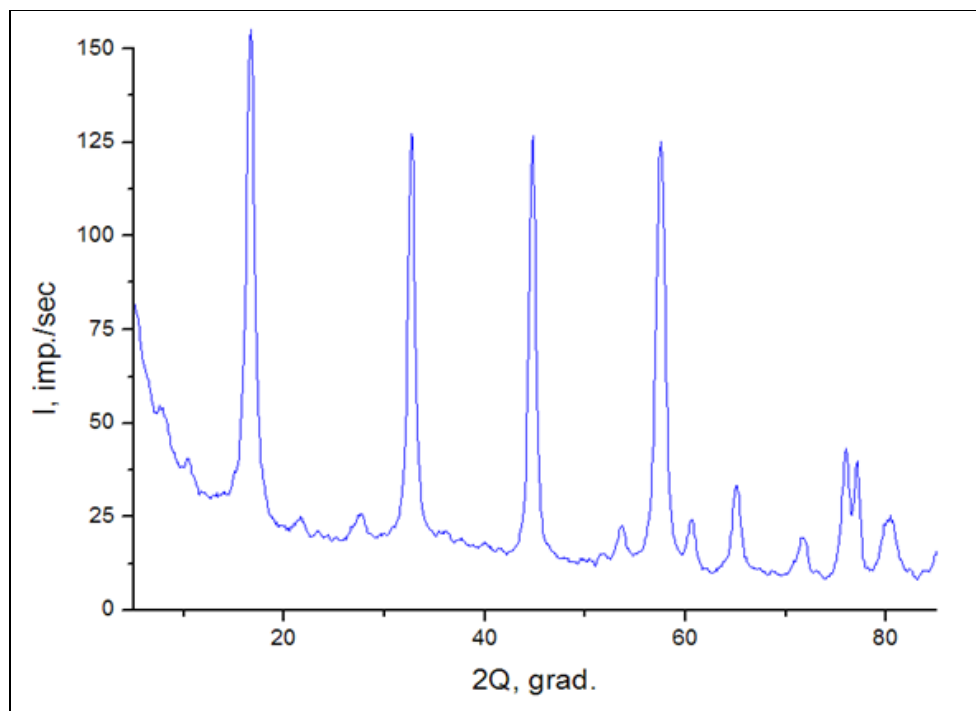


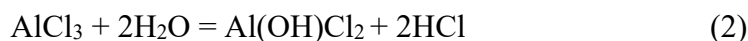
Figure 1. XRD patterns of samples produced in joint hydrolysis of carbamide and 20 % solution of AlCl_3 with a molar ratio $\text{AlCl}_3/(\text{NH}_2)_2\text{CO} = 0.67$ (stoichiometry).

The results showed that the use of carbamide as an accelerating hydrolysis additive is the most effective way to carry out the process of hydrothermal hydrolysis, in which not only a high, almost close to theoretical (more than 99.5 %) yield of boehmite is achieved, but also boehmite samples obtained during the hydrolysis process possess unique textural characteristics of interest for creating nanomaterials of various purposes on their basis.

3.2. Hydrolysis in Solid Phase

The study of the possibility of carrying out the process of hydrothermal hydrolysis AlCl_3 without the introduction of additives accelerating the hydrolysis is of particular interest. The analysis of thermodynamic data conducted by us for the conditions of the hydrothermal process showed that in order to enhance the efficiency of the hydrolysis, it is necessary to increase the concentration of the initial aqueous solution of aluminum chloride hexahydrate in our proposed method with removal of hydrogen chloride from the reaction zone.

Thus, the release of HCl at $T = 453\text{--}473\text{ K}$ and pressures of 0.8– 2.0 MPa is possible only when the concentration of HCl in the solution exceeds the concentration of HCl at the azeotrope point (which corresponds to 18 – 20 wt.%), while only water vapor is removed from the reaction zone before reaching this point. Assuming that the hydrolysis has passed on the second stage:



To achieve the azeotrope point, it is necessary to evaporate the initial solution at least two foldly. It is practically necessary to evaporate much more, because hydrolysis of the 2nd stage does not occur completely. Obviously, the maximum effect of the emission of HCl is possible at maximum concentrations of AlCl_3 . In this regard, we conducted experiments on the self-hydrolysis of aluminum chloride hexahydrate in the solid phase using crystalline hydrate water.

As it turned out, at a temperature of 453 - 513 K and a pressure of 0.45-2.3 MPa, the process of hydrothermal self-hydrolysis of crystalline aluminum chloride hexahydrate can be carried out by removing HCl from the reaction zone (Table 1), with producing of bayerite as the main product.

Table 1. Self-hydrolysis of solid aluminum chloride hexahydrate.

No.	Weight of AlCl ₃ ·6H ₂ O, g	T, K	Pressure, MPa	Hydrolysis time, h	Bayerite yield, %
1.	15	453	0.44	8	2.5
2.	15	473	1.5	3	2.3
3.	15	493	0.5	3	8.2
4.	15	493	1.5	3	29.7
5.	15	493	2.3	8	49.7
6.	15	513	1.5	3	54.0
7.	15	493	2.3	12	73.3
8.	15	513	1.5	8	~100.0

Analysis of the products of self-hydrolysis of aluminum chloride hexahydrate, carried out by NMR spectroscopy, showed that the water-insoluble part of the product is almost pure bayerite, and the soluble part is a mixture of aluminum oxychlorides (Fig. 2).

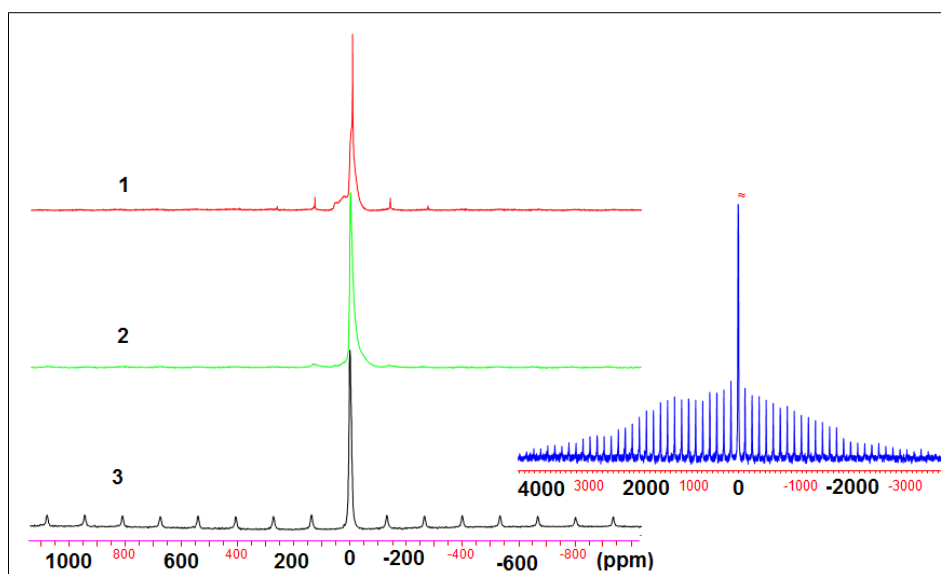


Figure 2. The ²⁷Al MAS NMR spectra (obtained on a Bruker Avance-400 spectrometer at a frequency of 104.2 MHz) of self-hydrolysis products of aluminum chloride hexahydrate (1, 2) and reference sample of bayerite (3).

4. Conclusions

Thus, the synthesis of aluminum oxyhydroxides (boehmite and bayerite) by hydrothermal hydrolysis of aluminum chloride hexahydrate in aqueous solutions and in the solid phase has been studied.

The complete hydrolysis of AlCl_3 occurs at a ratio $\text{AlCl}_3/(\text{NH}_2)_2\text{CO} = 0.67$ at a temperature of 433-513 K and a pressure of 0.6 - 2.4 MPa in aqueous solutions with the yield of 100 % a highly dispersed $\gamma\text{-AlOOH}$ (boehmite).

The possibility of hydrothermal self-hydrolysis of aluminum chloride hexahydrate with the removal of HCl from the reaction zone to produce bayerite was established for the first time. The most effective process of self-hydrolysis takes place at a temperature of 513 K and a pressure of 1.5 MPa. While bayerite is the main product of the self-hydrolysis of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in solid phase.

In all cases, the total content of Cl in the products of hydrolysis does not exceed 4 % wt.

5. Acknowledgements

This work was conducted within the framework of budget project No. AAAA-A17-117041710077-4 for Boreskov Institute of Catalysis.

The authors are also grateful to Prof. O. Lapina, Ph.D. Kh.Khabibulin, Ph.D. V. Ushakov and leading engineer I. Kraevskaya I.L. for the assistance in carrying out the study.

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